Lecture 14

Transmission Electron Microscope

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Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.

The first TEM was built by Max Kroll and Ernst Ruska in 1931, with this group developing the first TEM with resolution power greater than that of light in 1933 and the first commercial TEM in 1939.
Comparison of LM and TEM

- Both glass and EM lenses subject to same distortions and aberrations.

- Glass lenses have fixed focal length, it requires to change objective lens to change magnification. We move objective lens closer to or farther away from specimen to focus.

- EM lenses to specimen distance fixed, focal length varied by varying current through lens.

LM: (a) Direct observation of the image; (b) image is formed by transmitted light.

TEM: (a) Video imaging (CRT); (b) image is formed by transmitted electrons impinging on phosphor coated screen.
Transmission Electron Microscope: Principle

Ray diagram of a conventional transmission electron microscope (top path) and of a scanning transmission electron microscope (bottom path). The selected area electron diffraction (SAED) aperture (Ap) and the sample or specimen (Spec) are indicated, as well as the objective (Obj) and projector (Proj) or condenser (Cond) lenses.

Positioning of signal detectors in electron microscope column.
Resolution in SEM and TEM

The spatial resolution of the SEM depends on the size of the electron spot, which in turn depends on both the wavelength of the electrons and the electron-optical system which produces the scanning beam. The resolution is also limited by the size of the interaction volume, or the extent to which the material interacts with the electron beam. The spot size and the interaction volume are both large compared to the distances between atoms, so the resolution of the SEM is not high enough to image individual atoms, as is possible in the shorter wavelength (i.e. higher energy) (TEM). Depending on the instrument, the resolution can fall somewhere between less than 1 nm and 20 nm. By 2009, The world's highest SEM resolution at high beam energies (0.4 nm at 30 kV) is obtained with the Hitachi S-5500.

In a TEM, a monochromatic beam of electrons is accelerated through a potential of 40 to 100 kilovolts (kV) and passed through a strong magnetic field that acts as a lens. The resolution of a modern TEM is about 0.2 nm. This is the typical separation between two atoms in a solid. This resolution is 1,000 times greater than a light microscope and about 500,000 times greater than that of a human eye.

More recently, advances in aberration corrector design have been able to reduce spherical aberrations and to achieve resolution below 0.5 Ångströms at magnifications above 50 million times. Improved resolution allows for the imaging of lighter atoms that scatter electrons less efficiently, such as lithium atoms in lithium battery materials. The ability to determine the position of atoms within materials has made the HRTEM an indispensable tool for nanotechnology research and development in many fields, including heterogeneous catalysis and the development of semiconductor devices for electronics and photonics.
Transmission Electron Microscopy

JEOL 2000-FX intermediate voltage (200,000 volt) scanning transmission research electron microscope (configured for both biological and physical sciences specimens)

- magnification: X 50 to X 1,000,000
- 1.4 Ångstom resolution (LaB6 source)
- backscattered and secondary electron detectors
- Gatan Digi-PEELS Electron Energy Loss Spectrometer, software and off axis imaging camera
- Kevex Quantum 10 mm² X-ray detector (detects elements down to boron), with spatial resolution to as little as 20 nanometers (on thin sections)
- IXRF X-ray analyzer with digital imaging capability, X-ray mapping, feature analysis and quantitative software.
- Gatan Be double-tilt analytical holder for quantitative X-ray work
- Gatan cryo-TEM specimen holder (to -150°C)
- $700,000 as currently configured at current prices

TEM sample support mesh "grid", with ultramicrotomy sections (Wikipedia, 2010).
Electrons that go through a sample

**Bright field:** Contrast - is formed directly by occlusion and absorption of electrons in the sample. Thicker regions of the sample, or regions with a higher atomic number will appear dark, whilst regions with no sample in the beam path will appear bright – hence the term "bright field".

**Diffraction contrast:** Contrast is formed by elastically scattered electrons - Incident electrons that are scattered (deflected from their original path) by atoms in the specimen in an elastic fashion (no loss of energy). Samples can exhibit diffraction contrast, whereby the electron beam undergoes Bragg’s scattering which in the case of a crystalline sample, disperses electrons into discrete locations in the back focal plane. *Utilization* – electrons passing through at a similar angle are scattered, these electrons can then be collated using magnetic lenses to form a pattern of spots; each spot corresponds to a specific atomic spacing (a plane). This pattern can then yield information about the orientation, atomic arrangements and phases present in the area being examined.

**Electron energy loss:** Contrast is formed by inelastically scattered electrons. *Utilization*: The inelastic loss of energy by the incident electrons is characteristic of the elements that were interacted with. These energies are unique to each bonding state of each element and thus can be used to extract both compositional and bonding.

TEM (+ HRSTEM) – What do we get?

- **Morphology** – size, shape, arrangement of particles on scale of atomic diameters

- **Crystallographic information** – from diffracted electrons, get arrangement and order of atoms as well as detection of atomic-scale defects

- **Compositional information** – Chemical identity, including redox speciation (distinguish Fe$^{2+}$ and Fe$^{3+}$ for instance)
Bright Field
Calculated vertical scans through a sphere: (a) a perfectly reflecting sphere in reflection microscope with aperture angle 30°; (a) a transparent sphere with refraction index of 1.05 and refraction index of surrounding liquid of 1.33 in transmission microscope with aperture angle 30°.
Image contrast is obtained by interaction of the electron beam with the sample. Several contrast effects play a role. In the resulting TEM image denser areas and areas containing heavier elements appear darker due to scattering of the electrons in the sample. In addition, scattering from crystal planes introduces diffraction contrast. This contrast depends on the orientation of a crystalline area in the sample with respect to the electron beam. Because of the high resolution of the TEM, atomic arrangements in crystalline structures can be imaged in large detail.

High resolution TEM image of a multi-walled carbon nanowire. The wire consists of segments, bounded by inner segment boundaries (From 2008 Koninklijke Philips Electronics N.V.).
Examination of polymer vesicles by using microscopy. The cryogenic transmission electron microscope images were used for size determination because regular transmission electron microscopy and atomic force microscopy influence the structure of the observed vesicles. (a) Cryogenic transmission electron micrograph of an ABA polymer vesicle. (Scale bar: 200 nm.) (b) Electron micrograph of a cluster of vesicles. (Scale bar: 50 nm.) (c) Atomic force micrograph of vesicles on mica in nontapping mode shows that a film of polymer is formed on the hydrophilic mica surface with vesicles located in the film. (Scale bar: 200 nm.)

http://www.phys.rug.nl/mk/research/98/hrtem_localprobe.html
Ex-situ transmission electron microscopy images of GaAs nanowires: (a) before burying; the striations reveal stacking faults; (b) after complete burying; the faults have disappeared; (c) high resolution image of the interface region after partial burying; dashes indicate the lateral boundary of the buried portion of the nanowire, which has transformed to cubic structure, whereas the upper portion has remained hexagonal.

http://www.phys.rug.nl/mk/research/98/hrtem_localprobe.html
TEM of Carbon nanotubes

Three selected systems represents the chemically modified CNT. First are surface thiolated MWCNT, second are 'peapods' made by sucking Dy$_3$N@C$_{80}$ metallo-fullerenes into SWCNT, forming the Dy$_3$N@C$_{80}$@SWCNT, third, the conventional C$_{60}$@SWCNT fullerene peapods, fluorinated by Xenon difluoride (XeF$_2$) up to 18% of F. The last of interesting systems is fluorinated C$_{60}$ peapods, where we show high degree of homogeneous fluorination across whole surface.

http://www.phys.rug.nl/mk/research/98/hrtem_localprobe.html
Crystal nanospheres of Ti dopped CeO2 nanoparticles

Figure: (a) Scanning electron microscopy image of single crystal nanospheres of Ti dopped CeO2 nanoparticles. (b) Transmission electron microscopy image of a single crystal CeO2 nanosphere enclosed by a thin shell of amorphous TiO2. (c) Molecular dynamic simulated structure of Ti dopped CeO2 nanosphere (Science 312 (2006) 1504).
Electron Diffraction
Simplified ray diagram (Abbe diagram) that shows simultaneous formation of the diffraction pattern and the corresponding real space image in a transmission electron microscope (TEM) (From Weirich *Electron Crystallography*, 235–257.).
Simplified ray diagram (Abbe diagram) that shows simultaneous formation of the diffraction pattern and the corresponding real space image in a transmission electron microscope (TEM) (From Weirich *Electron Crystallography*, 235–257.).
Thin Lenses; Ray Tracing

Thin lens equation

\[ \frac{1}{d_o} + \frac{1}{d_i} = \frac{1}{f} \]
Focusing of the inclined parallel rays by a thin lens.
X-Ray Diffraction of Crystals and Symmetry

Incident plane wave

\[ A = A_o \exp[i(\vec{k}_o \vec{r} - \omega t)] \]

Scattered spherical wave

\[ A = \frac{C}{r_j} A_o \exp(ik_o \vec{\rho}_j) \exp[i(\vec{k}_i \vec{r}_i - \omega t)] \quad \text{where} \quad \vec{r} = \vec{R} - \vec{\rho}_j \]

The field in the point R

\[ A = A_o \frac{C}{R} \exp(i(kR)) \exp[i(\vec{k}_o - \vec{k}) \vec{\rho}_j] \exp(-i\omega t) \quad |r| \approx |R| \]

\[ A = A_o \frac{C}{R} \exp[i(\vec{k}_o - \vec{k}) \vec{\rho}_j] \exp[i(\vec{k}R - \omega t)] \]
X-Ray Diffraction of Crystals and Symmetry

\[ A = A_o \frac{C}{R} \exp[i(k_o - \vec{k})\vec{\rho}_j] \exp[i(\vec{k}R - \omega t)] \]

\[ \Delta \vec{k} = \vec{k} - k_o \]

\[ A = \frac{B}{R} \exp[-i\Delta \vec{k}\vec{\rho}_j] \quad \vec{\rho}_j = u\vec{a} + v\vec{b} + w\vec{c} \quad \text{direct lattice} \]

\[ A(R) = \frac{B}{R} \sum_{u,v,w} \exp[-i\Delta \vec{k}(u\vec{a} + v\vec{b} + w\vec{c})] \quad \text{max} \]

\[ \Delta \vec{k}(u\vec{a} + v\vec{b} + w\vec{c}) = 2\pi N \]

If \( \vec{G} \) is reciprocal vector

\[ a^* = \frac{[\vec{b} \vec{c}]}{V}; b^* = \frac{[\vec{c} \vec{a}]}{V}; c^* = \frac{[\vec{a} \vec{b}]}{V}; \quad \vec{G} = h\vec{a}^* + k\vec{b}^* + l\vec{c}^* \]
The Reciprocal Lattice

- The reciprocal lattice is constructed as follows:
- Choose a point to be the origin in the crystal lattice.
- Let the vector normal to a set of lattice planes in the real lattice radiate from that origin point such that the distance of the vector is the reciprocal of the d spacing for each family of planes. i.e. the vector for the plane \((hkl)\) has a distance of \(1/d_{(hkl)}\) (or, more generally \(K/d_{(hkl)}\)).
- Repeat for all real lattice planes.

\[
\mathbf{a}^* = \frac{bc \sin \alpha}{a^2}; \quad \mathbf{b}^* = \frac{ac \sin \beta}{a^2}; \quad \mathbf{c}^* = \frac{ab \sin \gamma}{a^2}
\]

It is possible to show that

\[
|\mathbf{G}_{hkl}| = \frac{1}{d_{hkl}}
\]
Consider a set of planes determined by Miller indices $hkl$, then

$$|\vec{G}_{hkl}| = \frac{1}{d_{hkl}}$$

$$|\Delta\vec{k}| = \frac{2\pi}{\lambda} 2\sin\theta_{hkl}$$

$$\frac{1}{d_{hkl}} = \frac{2\sin\theta_{hkl}}{\lambda}$$

$$n\lambda = 2d_{hkl} \sin\theta_{hkl}$$
Real Space versus Reciprocal Space

Real space:
- $x, y, z$

Reciprocal space:
- $k_x, k_y, k_z$

$k_x = \frac{2\pi}{\Delta x}$

$\Delta x =$ row spacing

$k_x \perp$ rows

Visible Light Laser

35mm slide

Projection Screen

Real space:
- $x, y, z$

Reciprocal space:
- $k_x, k_y, k_z$
The Reciprocal Lattice

Because of the reciprocal nature of $d$ spacings and $q$ from Bragg’s Law, the pattern of the diffraction we observe can be related to the crystal lattice by a mathematical construct called the \textit{reciprocal lattice}. In other words, the pattern of X-ray reflections makes a lattice that we can use to gain information about the crystal lattice.
Calculation of the phase difference of the waves scattered from two lattice points.
Crystallographic Image Processing (CIP) of high-resolution electron microscopy (HREM) images. (a) HREM image of α and β-Ti₂Se recorded with a 300 kV TEM (Jeol 3010UHR, point resolution 1.7 Å) along the [001] zone axis. (b) Fourier transform (power spectrum) of the HREM image (only the amplitudes are shown). The position of the white ring marks the first crossover of the Contrast Transfer Function (CTF) which is used to determine the defocus value. The structure factor phases of all reflections outside the white ring have a phase difference of 180 compared to their true value.

The latter causes inversion of image contrast. (c) Lattice averaged image (p2 symmetry) deduced from the amplitudes From Fourier Series Towards Crystal Structures 247 and phases in the power spectrum before CTF-correction. (d) Projected pseudo-potential map (p2gg symmetry) after correction of the phase-shifts imposed by the CTF showing all columns of atoms in black. The average agreement of atomic co-ordinates determined from the pseudo-potential map and the superimposed model from X-ray diffraction is about 0.2 Å. (filled circle = Ti; open circle = Se ). (K. Albea, T. E. Weirich Acta Crystallographica. A, 2002)
Graphene-Based Polymer Nanocomposites

HRTEM and SAED Patterns of Graphene Nanocomposites

- TEM used to determine if the graphene-based sheets were present as exfoliated sheets or multi-layered platelets
- Electron diffraction patterns and $d$ spacings as well as high resolution TEM suggest that platelets are individual graphene sheets randomly dispersed in the polymer matrix
- High resolution TEM shows regions where fringes are observed and regions where they are not indicating significant local curvature in the graphene sheets

Focused Ion Beam (FIB) TEM sample preparation

Sketch of the model of the subsurface defect in Cr-DLC film

SEM images of the defect BLD#C: (a) Defect C prior to sputtering, SEM image with 60° tilt; (b) Defect BLD#C after sputtering. The depth of the trench is approximately 1.9 µm. P1a denotes a distance between two crosses P1 and PR1.
Focused Ion Beam Sample Preparation for TEM/EELS measurements

SEM image of the small wedge of the $c$-BC$_3$ phase removed by focused ion beam (FIB) instrument.

Outside half of the sample has been thinned to electron transparency. After additional ion milling to remove damage-09, thickness is estimated at \( \sim 50 \text{ nm} \).
Electron Diffraction of c-BC$_3$ Phase

Low magnification image of final section on TEM half grid.

Diffraction pattern. Internal calibration provided by FIB-deposited Pt layer.
Electron Energy Loss Spectroscopy (EELS)
In general Electron Energy Loss Spectroscopy bases on the energy losses of electrons when inelastically scattered on matter. An incident beam of electrons with a known energy ($E_i$) is scattered on a sample. The scattering of these electrons can excite the electronic structure of the sample. If this is the case the scattered electron loses the specific energy ($\Delta E$) needed to cause the excitation. Those scattering processes are called inelastic.

It may be easiest to imagine that the energy loss is for example due to an excitation of an electron from an atomic $K$-shell to the $M$-shell. This energy for this excitation is taken away from the electrons kinetic energy. Then the energies of the scattered electrons ($E_s$) are measured and the energy loss can be calculated. From the measured data an intensity versus energy loss diagram is established. In the case of scattering on phonons the so called energy loss can also be a gain of energy.

These energy losses allow, using comparison to other experiments, or theory, to draw conclusion about surface properties of the sample (Wikipedia 2006).
Fine structures in an electron energy-loss (EEL) spectrum originate in the transition of electrons from a core level to unoccupied states under the dipole selection rule, therefore energy-loss near edge structure (ELNES) includes the detailed information of a electronic structure of a material.

Chemical analysis

Changes in chemical bonding produce changes in the shape of EELS edges

- Fingerprinting is the technique of identifying a chemical structure from the edge shape
- Quantification is possible with references

![Graphs showing energy-loss vs. energy for different compounds: O₂, MnO, Fe₂O₃, CoO, NiO.](image)
Diamond, graphite and fullerene are the matters which consists of only carbon, so that, all of these specimens have absorption peaks around 284 eV in EELS corresponding to the existence of carbon atom. From the fine structure of the absorption peak, the difference in bonding state and local electronic state can be detected. The sharp peak at absorption edge corresponds to the exitation of carbon K-shell electron (1s electron) to empty anti-bonding pi-orbital. It is not observed for diamond, because of no pi-electron in it.
Incorporation of BN nanodomains in a bundle of C SWNT.

Left: EELS elemental mapping of C, B and N.

Right: Atomic structure simulations for two types of domains with preferential N and B along the rims, the first ones being shown to be more stable.

Colliex et al., Acta Microscopica 16 (1-2) 2007
Incorporation of B in a bundle of C SWNT.

Representative high-resolution TEM micrographs of boron-doped SWCNT. The dots in the micrograph (see arrows) depict the position used for the EELS analysis of the substitution level.

Typical EELS spectrum of the position indicated by the dashed line in the profile concentration, which is presented in the inset.

High-resolution EELS core level excitation spectra of B-doped SWCNT in the range of the B1s, C1s and N1s edges.

Incorporation of BN nanodomains in a bundle of C SWNT.

(a) TEM image, EELS spectra of carbon; (b) C-K and (c) nitrogen, N-K in the graphitic C$_3$N$_4$ phase.
<table>
<thead>
<tr>
<th><strong>EDXS and EELS comparisons</strong></th>
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<tr>
<td><strong>(S)TEM EDS X-ray</strong></td>
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<tr>
<td>X-rays provide elemental information only</td>
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<tr>
<td>Inefficient signal collection; inefficient low Z signal generation &amp; detection</td>
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<tr>
<td>✗ Slow mapping or poor S/N</td>
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<tr>
<td>✗ X-ray spectra can contain artifact information from column and other parts of sample</td>
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<tr>
<td>High detection efficiency for higher Z elements</td>
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<tr>
<td>✗ Poor sensitivity to Z&lt;10</td>
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<tr>
<td>✗ Energy resolution &gt; 120eV causes frequent overlaps</td>
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<tr>
<td>✗ No sample thickness limitations</td>
</tr>
<tr>
<td>✗ Sample thickness is important - should be less than ~100nm @ 200keV</td>
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</table>
The Scale of Things – Nanometers and More

Things Natural

- Ant: ~5 mm
- Fly ash: ~10-20 μm
- Human hair: ~60-120 μm wide
- Red blood cells: (~7-8 μm)
- Dust mite: 200 μm
- Pollen grain
- Red blood cells
- DNA: ~2-1/2 nm diameter
- Atoms of silicon: spacing 0.078 nm

Things Manmade

- Head of a pin: 1-2 mm
- MicroElectroMechanical (MEMS) devices: 10-100 μm wide
- Carbon buckyball: ~1 nm diameter
- Nanotube electrode: ~1.3 nm diameter
- Quantum corral of 48 iron atoms on copper surface: positioned one at a time with an STM tip
  - Corral diameter: 14 nm

The Challenge

Fabricate and combine nanoscale building blocks to make useful devices, e.g., a photosynthetic reaction center with integral semiconductor storage.

The Scale of Things – Nanometers and More

Microworld

- 1 cm = 10 mm
- 1,000,000 nanometers = 1 millimeter (mm)
- 10^-3 m = 100 μm
- 10^-4 m = 10 μm
- 10^-5 m = 1 μm
- 1,000 nanometers = 1 micrometer (μm)

Nanoworld

- 10^-6 m = 100 nm
- 10^-7 m = 10 nm
- 10^-8 m = 1 nm

Soft x-ray

Visible

Infrared

Microwave

The Scale of Things – Nanometers and More

- 10^-9 m = 0.1 nm
- 10^-10 m = 0.01 nm
- 10^-11 m = 0.1 nm
- 10^-12 m = 1 nm

- 1,000,000 nanometers = 1 mm
- 1 mm = 1000 μm
- 1 μm = 1000 nm
- 1 nm = 1000 Å

- 10^-3 m = 1 mm
- 10^-4 m = 1000 μm
- 10^-5 m = 100 μm
- 10^-6 m = 10 μm
- 10^-7 m = 1 μm
- 10^-8 m = 0.1 μm
- 10^-9 m = 10 nm
- 10^-10 m = 1 nm

- 10^-11 m = 0.1 nm
- 10^-12 m = 0.01 nm
- 10^-13 m = 0.1 nm
- 10^-14 m = 1 nm

- 10^-15 m = 10 nm
- 10^-16 m = 100 nm
- 10^-17 m = 1 μm
- 10^-18 m = 1 mm

- 10^-19 m = 1 cm
- 10^-20 m = 10 mm
- 10^-21 m = 100 μm
- 10^-22 m = 1 μm
- 10^-23 m = 1 nm
- 10^-24 m = 10 nm
- 10^-25 m = 100 nm
- 10^-26 m = 1 μm
- 10^-27 m = 1 mm
- 10^-28 m = 1 cm

- 10^-29 m = 10 mm
- 10^-30 m = 100 μm
- 10^-31 m = 1 μm
- 10^-32 m = 1 nm
- 10^-33 m = 10 nm
- 10^-34 m = 100 nm
- 10^-35 m = 1 μm
- 10^-36 m = 1 mm
- 10^-37 m = 1 cm

Dust mite

Carbon nanotube

Microworld

Nanoworld

- 10^-3 m = 1 mm
- 10^-6 m = 100 nm
- 10^-9 m = 1 nm

- 1 nm = 10 Å
- 100 nm = 1000 Å
- 1 μm = 1000 nm
- 1 mm = 1000 μm
- 1 cm = 100 mm

- 1 nm = 10 Å
- 100 nm = 1000 Å
- 1 μm = 1000 nm
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- 1 cm = 1000 mm

- 1 nm = 10 Å
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- 1 mm = 1000 μm
- 1 cm = 1000 mm
General References


Center for Advanced Materials Characterization in Oregon (Facilities): http://epmalab.uoregon.edu/lecture.htm